

Title: APPARATUS AND METHOD FOR TREATMENT OF METAL SURFACES
BY INORGANIC ELECTROPHORETIC PASSIVATION

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TECHNICAL FIELD

The present invention relates to inorganic electrophoretic passivation of conductive surfaces and, more particularly, to a method for prevention of additive oxidation and anode film build-up in apparatus while carrying out processes of inorganic electrophoretic passivation of such conductive surfaces.

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BACKGROUND OF THE INVENTION

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In a conventional electrolytic process for forming a passivating deposit on or for priming the surface of a conductive substrate, such as a metallic or other conductive surface, electromotive force is applied to deposit a mineral-containing coating or film on a metallic or conductive surface. The conductive substrate is placed in an electrolytic cell containing a solution of the mineral-containing coating or film precursor and other additives, and is connected to an electrical circuit including an anode and a cathode. In the circuit, the conductive substrate forms the cathode, and the anode is formed of, e.g., a relatively inert or noble metal, such as platinum, platinum coated niobium or platinum coated nickel. The current is applied at a voltage and current density appropriate to deposit the mineral-containing coating or film on, or to prime for subsequent coating, the metallic or conductive surface of the substrate.

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As will be understood, the application of such current results in electrolysis of materials (e.g., water) at the anode, including oxidation, as well as reduction of materials at the cathode. For example, oxygen gas may be produced at the anode by electrolysis of water, and hydrogen gas may be produced at the cathode. As one result of the oxygen production, other additives in the solution and/or the anode itself may be oxidized. Some of the products of this oxidation may be deposited on the anode, thus interfering with and reducing

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current flow. For this reason a relatively inert or noble metal is conventionally required in order to avoid oxidation of the anode metal. The relatively inert or noble metals useful in the conventional system are relatively expensive.

5 However, use of such anode metal does not completely alleviate the problem of accumulation of deposits on the anode in a conventional process. For example, silica from a silica-containing electrolytic solution can deposit on the anode surface. In addition, additives in the solution which are oxidized by the oxygen generated by the anode current may accumulate on the anode surface or the anode surface itself may be oxidized. As a result, even when one of the known
10 relatively inert or noble metals is used as the anode in a conventional process, the anode must be cleaned on at least a daily basis in order to remove accumulated oxidation products and materials resulting from the oxidation taking place at the anode. In the conventional system, if less expensive metals are substituted for the relatively inert or noble metals, the less expensive metals may
15 be quickly oxidized by the oxidizing conditions at the anode.

Accordingly, a need exists for an apparatus and a process for depositing a silica-containing mineral on a metallic or other conductive surface for, e.g., passivating or priming the metal surface, which avoids or reduces such problems. That is, a need exists for such a process which can proceed without
20 one or more of deposition on the anode, oxidation of additives, precipitation or fouling out of additives, or oxidation of anode materials.

SUMMARY OF THE INVENTION

25 The present invention relates to an apparatus and a process for electrolytically treating a metal surface. The apparatus includes an electrochemical cell which includes an anodic chamber, a cathodic chamber, and a divider separating the anodic chamber from the cathodic chamber. The anodic chamber has an anode and contains a conductive anodic medium. The cathodic chamber has, as a cathode, the metal surface to be treated, and contains a

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conductive cathodic medium including a silica-containing mineral composition. In one embodiment, during operation of the apparatus, the anode remains substantially free of accumulation of foreign materials. In one embodiment, the anode itself is not substantially oxidized. In another embodiment, during
5 operation of the apparatus, the conductive cathodic medium remains substantially free of oxidation by the anode. In one embodiment, the conductive anodic medium is free of oxidizable organic or inorganic additives. In one embodiment, the treating comprises passivation of the metal surface. In another embodiment, the treating comprises priming of the metal surface.

10 The present invention further relates to a process for electrolytically treating a metal surface. In one embodiment, the process passivates the metal surface. The process includes, inter alia, providing a metal surface and providing an electrochemical cell. The electrochemical cell includes an anodic chamber having an anode disposed therein, and containing a conductive anodic
15 medium; a cathodic chamber in which the metal surface may be disposed as a cathode, and containing a conductive cathodic medium comprising a silica-containing mineral composition; and a divider disposed to separate the anodic chamber from the cathodic chamber. In the process, an electric current is applied to the electrochemical cell at a rate and period of time sufficient to treat
20 the metal surface. In one embodiment, during the applying, the anode remains substantially free of accumulation of foreign materials. In another embodiment, during the applying, the conductive cathodic medium remains substantially free of oxidation by oxygen generated at or by the anode. In one embodiment, the conductive anodic medium is free of oxidizable organic or inorganic additives. In
25 one embodiment, the treating comprises depositing a silicon-containing mineral on the metal surface. In one embodiment, the treating comprises passivation of the metal surface. In another embodiment, the treating comprises priming of the metal surface.

In accordance with the foregoing, as explained in detail in the following, the present invention provides an apparatus and a method which can proceed without one or more of deposition on the anode, oxidation of additives, precipitation or fouling out of additives, or oxidation of anode materials.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic depiction of an electrolytic cell in accordance with one embodiment of the present invention.

10 Fig. 2 is a schematic depiction of an electrolytic cell in accordance with another embodiment of the present invention.

Fig. 3 is a schematic depiction of an electrolytic cell in accordance with yet another embodiment of the present invention.

Fig. 4 is a schematic depiction of an electrolytic cell in accordance with still another embodiment of the present invention.

15 Fig. 5 is an enlarged view of a container formed by an embodiment of the divider.

It should be appreciated that for simplicity and clarity of illustration, elements shown in the Figures have not necessarily been drawn to scale. For example, the dimensions of some of the elements may be exaggerated relative to each other for clarity. Further, where considered appropriate, reference numerals have been repeated among the Figures to indicate corresponding elements.

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It should be appreciated that the process steps and structures described below do not form a complete process flow for treating a metal surface or other conductive surface. The present invention can be practiced in conjunction with techniques currently used in the art, and only so much of the commonly practiced process steps are included as are necessary for an understanding of the present invention.

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DETAILED DESCRIPTION

The present invention relates to an apparatus and a process for treating a metal or electrically conductive surface, for example, by depositing a silica-containing mineral, in one embodiment in the form of a coating or film, on the metal or electrically conductive surface. While the invention is primarily adapted for use with metal or metallic surfaces, it should be understood that any

The following description refers to a metal surface, but it should be understood that as used herein, the term "metal surface" includes generally conductive surfaces, be the surface metal, metallic, polymeric coated with metal, carbon or graphite, or other conductive material, such as a conductive polymer. The term "metal surface" as used herein includes a wide range of metal surfaces such as steel, silicon-containing steel, iron and iron alloys, zinc, copper, lead, metallized ceramics and plastics, conductive polymers, carbon and graphite, among other metals and alloys thereof. The metal-containing surface may also include naturally occurring or man-made oxidation and reduction products, e.g., Fe_3O_4 , Fe_2O_3 , among others.

The silica-containing mineral deposit, in one embodiment, comprises a silica-containing material. As described herein, the silica-containing material, in one embodiment, is obtained from a silica compound. In one embodiment, the silica compound is a silicate.

The process employs a silica-containing mineral composition in the conductive cathodic medium, e.g., the conductive cathodic medium contains soluble silica-containing mineral components, and utilizes an electrolytic process to obtain a silica-containing mineral deposit upon the metal surface. In one embodiment, the deposit is in the form of a coating or film. The term "silica-containing mineral deposit," refers to a relatively thin deposit, coating or film which is formed upon the metal surface, in which at least a portion of the deposit, coating or film includes at least one silica-containing mineral, for example, an

amorphous phase or matrix comprising a silicate. In one embodiment, the thickness of the coating or film ranges from about 10 angstroms to about 10,000 angstroms, and in another embodiment from about 100 angstroms to about 2500 angstroms.

5 In the foregoing disclosure, as well as in the following disclosure and in the claims, the numerical limits of the disclosed ranges and ratios may be combined. Thus, for example, in the preceding thickness range, although not explicitly stated, the disclosure includes ranges from about 100 angstroms to about 10,000 angstroms and from about 10 angstroms to about 2500 angstroms.

10 The terms "electrolysis", "electrolytic", or similar or cognate terms, refer to a process including passing an electrical current from an anode through a conductive cathodic medium containing, e.g., a silica-containing mineral composition, while the conductive cathodic medium is in contact with an electrically conductive substrate, e.g., the metal surface, in which the substrate
15 functions as the cathode. In general, electrolysis is a process that decomposes a chemical compound into its elements or produces a new compound by the action of an electrical current. The electrical current is passed through the electrolytic cell and chemical reactions based on oxidation/reduction, acid/base, pH, precipitation, heated-driven or siccative conditions occur at the electrodes,
20 i.e., at the anode and/or cathode.

The apparatus includes an electrolytic cell including an anode chamber and a cathode chamber and a divider separating these cells. In general, the metal surface to be treated will be immersed in the cathodic chamber, and will act as the cathode in the electrolytic process.

25 Fig. 1 is a schematic depiction of an apparatus 100 for electrolytically treating a metal surface, in accordance with a first embodiment of the present invention. The apparatus 100 includes an electrolytic cell 110, having an anodic chamber 112 and a cathodic chamber 114. The anodic chamber 112 is separated from the cathodic chamber 114 by a divider 116. The divider 116

allows electrical current and, in some embodiments, allows selected ions to pass through the divider 116, but prevents the passage of other ions and molecules.

As shown in Fig. 1, in the anodic chamber 112 there is disposed an anode 118, which is immersed in a conductive anodic medium 120. In accordance with one embodiment of the invention, the anode 118 may be formed of an active, inexpensive metal such as iron, etc. In accordance with this embodiment of the present invention, because the anodic chamber 112 is separated from the cathodic chamber 114, it is not necessary that the anode be coated with or be formed of an inert or relatively unreactive metal, as in the prior art.

As noted, the present invention enables the use of less expensive, more active metals as the anode(s), while at the same time avoiding release of ions of the anode material into the medium and thence deposition thereof onto the metal surface. While in the prior art, anodes were required to be composed of or covered by an inert or noble metal, for example, niobium or nickel plated with platinum, in an electrolytic cell according to the present invention, a much wider variety of metals may be employed as the anode. In one embodiment of the present invention, the anode comprises an active metal free of protection by a noble metal. In one embodiment, the anode comprises an uncoated active metal. Thus, for example, the anode of the present invention may be formed of, e.g., uncoated or unprotected iron, zinc, tin, nickel, steel, Monel®, titanium, or graphite, or any of the metals disclosed below for use as the metal surface at the cathode, which would otherwise possibly contaminate the cathode metal surface with anode-derived metal atoms. In one embodiment of the present invention, the anode metals may be prevented from depositing on the cathode metal surface. In another embodiment, such as when an ion-selective divider is used, a metal from the anode may be controllably allowed to deposit on the cathode metal surface.

In one embodiment, the anode 118 may be in the form of a plate or any other suitable shape, as known in the art. As described below, in other

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embodiments, the anode may be conformal, either partially surrounding or conforming to a divider; the anode may be surrounded by a divider; or the anode may be substantially covered or coated by a divider. In one embodiment, more than one anode may be used, as needed. The anode shape and number may
5 be suitably selected as needed based on factors such as the current density, the configuration of the electrochemical cell, the chemistry of the conductive medium and other factors known to those of ordinary skill in the art.

The anodic chamber 112 contains a conductive anodic medium 120. The only limiting criteria for the anodic medium is that it be conductive of an electrical
10 current. The conductive anodic medium 120 may be acidic, neutral or basic. In one embodiment, the conductive anodic medium 120 is acidic, i.e., has a pH less than 7. In one embodiment, the anodic medium has a pH in a range from about 2 to about 6, and in another embodiment, a pH in a range from about 3 to about 5. In one embodiment, the conductive anodic medium 120 has a basic pH, i.e.,
15 has a pH greater than 7. In one embodiment, the conductive anodic medium 120 has a pH of 9 or greater. In another embodiment, the conductive anodic medium 120 has a pH of 11 or greater.

The conductive anodic medium 120 contains suitable acids, bases, salts and/or buffering agents to attain the selected pH. Persons of ordinary skill in the
20 art can determine and select the appropriate combination of acids, bases, salts and/or buffering agents to attain the selected pH. In one embodiment, the conductive anodic medium comprises an aqueous solution of an alkali or alkaline earth metal hydroxide. In one embodiment, the conductive anodic medium comprises an aqueous solution of sodium hydroxide or potassium hydroxide. In
25 one embodiment, the conductive anodic medium comprises from about 1 wt% to about 50 wt% of an alkali or alkaline earth metal hydroxide. In another embodiment, the conductive anodic medium comprises from about 3 wt% to about 25 wt% of an alkali or alkaline earth metal hydroxide. In another embodiment, the conductive anodic medium comprises from about 5 wt% to

about 15 wt% of an alkali or alkaline earth metal hydroxide. In another embodiment, the conductive anodic medium comprises from about 6 wt% to about 10 wt% of an alkali or alkaline earth metal hydroxide.

As described in more detail below, in one embodiment, the conductive anodic medium 120 in the anodic chamber 112 is free of oxidizable organic or inorganic additives. In one embodiment, the conductive anodic medium in the anodic chamber is free of oxidizable organic or inorganic compounds. "Free of oxidizable organic or inorganic compounds" means that the conductive anodic medium contains substantially no oxidizable organic or inorganic compounds, from any source other than impurities and other inadvertently present species. In one embodiment, the conductive anodic medium in the anodic chamber is free of oxidizable organic additives. "Free of organic additives" means that no organic additives are intentionally placed or included in the conductive anodic medium.

The conductive anodic medium may be prepared by simply dissolving the acid, base, buffering agents and any other ingredients in water, with appropriate temperature control as needed to facilitate dissolution.

As shown in Fig. 1, in the cathodic chamber 114 there is disposed an object 122, which is immersed in a conductive cathodic medium 124. In accordance with an embodiment of the present invention, the object 122 includes a conductive metal surface. As noted above, the conductive metal surface acts as the cathode in the apparatus shown in Fig. 1. In accordance with an embodiment of the present invention, the conductive cathodic medium 124 includes a silica compound, as described in more detail below. The object 122 is depicted in Fig. 1 in the form of a bolt or screw, but the invention is not limited to such an object or to any object in particular. As noted above, the object may be any object which includes a conductive metal surface.

The conductive cathodic medium 124, as noted, includes a silica-containing mineral composition. In one embodiment the silica-containing mineral

ATOTP0107A

composition contains a water dispersible silica compound or mixture of such compounds, and in one embodiment, the silica compound or mixture is at least partially water soluble. In one embodiment, the silica-containing mineral composition is electrolytically deposited on the metal surface of the object 122, in order to treat the metal surface. In one embodiment, a chemical bond is formed between atoms of the metal surface and the silica-containing mineral composition. In one embodiment, the treating is passivating the metal surface, and in another embodiment, the treating is priming the metal surface. In other embodiments, other suitable treatments may be applied to the metal surface, as known in the art.

In one embodiment, the conductive cathodic medium 124 includes a colloidal silica compound. In one embodiment, the colloidal silica includes a silicate. In one embodiment, the silicate is a sodium silicate. Sodium silicates include silicates have formulae such as Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_7$ or $\text{Na}_2\text{Si}_3\text{O}_7$, with variable amounts of water of hydration.

In one embodiment, the conductive cathodic medium 124 comprises at least one silica- or silicate-containing compound or precursors thereof, and may be referred to as a silica-containing mineral composition. The terms silica- and silicate-containing are used interchangeably herein. Examples of such silica-containing mineral compositions comprise at least one member chosen from the group of silica, boro-silicates, magnesium silicate, calcium silicate, potassium silicate, sodium silicate, magnesium silicate, tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), silicones, siloxanes, kaolin, Al--Na (SiO_2) complex oxides, sodium aluminate, silanes, partially hydrolyzed ethyl ortho silicate and its reaction products formed with quaternary ammonium compounds (e.g., cetyltrimethyl ammonium bromide in ethyl alcohol), iron silicate, tetra alkyl ammonium salts of silica acids, precursors thereof, among others. In one embodiment, the silica-containing mineral composition includes colloidal silica that is stabilized with, e.g., sodium aluminate, ammonium ion, or alumina, that

ATOTP0107A

contains ethyl glycol, or other known stabilization additives and treatments (such materials are included in aqueous solutions commercially available, such as Ludox®). In one embodiment, the amount of silica-containing mineral composition comprises from about 3 wt% to about 65 wt%, or from about 5 wt% to about 50 wt%, or from about 10 wt% to about 35 wt%, of the conductive cathodic medium 124. In an embodiment in which the silica-containing mineral composition comprises a silicate such as sodium silicate, the cathodic medium will have a basic pH. In one embodiment, the cathodic medium has a pH in the range from about 8 to about 13. In one embodiment, the cathodic medium has a pH in the range from about 9.5 to about 11.5. In another embodiment, the cathodic medium has a basic pH which ranges up to about 14.

In one embodiment, the cathodic medium has an acidic pH in the range from about 2 to about 7, and in another embodiment, the cathodic medium has a pH in the range from about 3 to about 5, and in another embodiment, the cathodic medium has a pH in the range from about 3.2 to about 4.5.

In one embodiment, the silica compound comprises a colloidal silica. Suitable colloidal silica is available from PQ Corp. Various grades of colloidal silica are available from Philadelphia Quartz (PQ) Corp., Valley Forge, PA. In one embodiment, the colloidal silica is "N" Grade silica from Philadelphia Quartz Corp., which also may be referred to simply as "PQN silica". In another embodiment, the colloidal silica is "M" grade from Philadelphia Quartz Corp.

In one embodiment, the colloidal silica comprises a colloidal silica such as a Ludox® silica, available from E.I. duPont de Nemours & Co., Inc. Various grades of Ludox® silica are available including, for example, Ludox® AM-30 (30% suspension in water), Ludox® L5, Ludox® A5-30, Ludox® CL, Ludox® TMA (34% suspension in water) and Ludox® SM-30. In one embodiment, the silica compound comprises Ludox® AM-30. Other sources and grades of colloidal silica may be suitable for use in the present invention, and other

ATOTP0107A

sources and grades of silica and silicates may be suitable for use with the present invention.

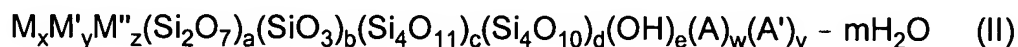
In one embodiment, the conductive cathodic medium may include a mixture of silica-containing materials. For example, in one embodiment, the conductive cathodic medium may include from about 1 wt% to about 15 wt% of a colloidal silica such as Ludox® AM-30, together with a colloidal silica such as PQN silica, in which the total loading of silica in the conductive cathodic medium is in a range from about 3 wt% to about 65 wt%. In another embodiment, the first colloidal silica (e.g., a Ludox® silica) is present in a range from about 2 wt% to about 10 wt%. In another embodiment, the total loading of silica in the conductive cathodic medium is in a range from about 5 wt% to about 50 wt%. In yet another embodiment, the total loading of silica in the conductive cathodic medium is in a range from about 10 wt% to about 35 wt%. In other embodiments, two colloidal silicas may be present in any relative amount, with a total loading in the above-disclosed ranges.

In one embodiment, the silica may be a water-soluble silicate. As the water-soluble silicate, for example, one represented by formula (I) may be suitable:



(wherein M is an alkali metal, or $-N(CH_2CH_2OH)_4$, $-N(CH_2CH_2OH)_4$, $-N(CH_2CH_2OH)_2$ or $-C(NH_2)_2NH$, and n is from 0.5 to 5). Such a water-soluble silicate may or may not include water of crystallization.

A convenient notation for describing the silicate compounds useful in the present invention is by use of the following general formula (II):



ATOTP0107A

wherein M, M' and M'' are ions of Group I, II and/or III metals, A and A' are independently silicates, molybdates, phosphates, zirconates, titanates, tungstates, vanadates, permanganate, pertechnetate, chromate, nitrate, carbonates, aluminates, ferrates, and mixtures thereof, among others; wherein
5 w, v, x, y and z each can be any number including zero but x, y and z cannot all be zero simultaneously; wherein a, b, c and d can each be any number including zero but cannot all be zero simultaneously; wherein mH_2O is the water of hydration and generally ranges from zero to about 10; and wherein e is an integer and generally ranges from zero to about 4. In one embodiment, when
10 the silicate compound represented by formula (II) has become bound to the metal surface, at least one of M, M' and M'' is a metal atom of which the metal surface is comprised. Often, in formula (II), one or more of M, M' and M'' is calcium, potassium or sodium.

Useful silica-containing mineral compositions are available from INEOS
15 Silicas, Joliet, Illinois. Such products include, for example, Metso™, Crystamet™, Drymet™ - metasilicates, Crystal™ and Silchem™ - silicate solutions, Crosfield™ K series - potassium silicate, Crosfield™ L series - lithium silicate, Croslink™, Crosfix™, Claysil™, Silacros™ - specialty silicates and Macrosorb™ - magnesium silicate. Sodium silicate is also available from INEOS
20 and is useful as a silica-containing mineral composition.

In one embodiment, one or more additional mineral components, which may be other metal compounds, may be present in the silica-containing mineral composition. In one embodiment, such other mineral components may include one or more of molybdenum, chromium, titanium, zirconium, vanadium,
25 phosphorus, aluminum, iron, boron, bismuth, gallium, tellurium, germanium, antimony, niobium, magnesium, manganese, tin and zinc and their oxides and salts. The additional mineral component is generally water soluble or dispersible within the conductive cathodic medium. In one embodiment, the additional mineral component is present in an amount ranging from about 0.001 wt% to

ATOTP0107A

about 5 wt%, and in another embodiment from about 0.01 wt% to about 1 wt%, based on the weight of the medium. Use of the additional mineral component may provide benefits such as enhancing the mineral layer formation rate, modifying the chemistry and/or physical properties of the resultant layer, as a diluent for the electrolyte or silicate containing medium, among others.

Various additives may be included in the conductive cathodic medium to aid in the treating of the metal surface. In one embodiment, organic or inorganic additives may be used, singly or in any suitable combination. In one embodiment, such additives, if exposed to the anode, may be subject to oxidation. Since these additives are confined to the cathodic chamber in the present invention, these additives may remain free of oxidation which might otherwise occur at or near the anode.

If desired, a wide range of additives can be included in the conductive cathodic medium such as viscosity control agents, for example, aliphatic polymer with carboxylic acid groups, such as CARBOPOL®, supplied by B.F. Goodrich, xanthan gum, silica, synthetic minerals such as LAPONITE®, supplied by Southern Clay Products, pH modifiers, for example, an alkaline material such as sodium hydroxide, potassium hydroxide, triethanolamine, ammonium hydroxide, buffering agents, dyes, surfactants, solvents, among other materials. In one embodiment, the amount of additive, when present, comprises from about 1 wt% to about 120 wt% of the silica-containing mineral in the medium.

Other additives may include, for example, various types of AEROSIL® (hydrophilic silicas), polysaccharides such as xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, relatively high molecular weight polyethylene glycol mono-esters and diesters of fatty acids, polyacrylates (such as the above-noted CARBOPOL® or SYNTHALENS® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols, for example pentaerythritol or trimethylol

ATOTP0107A

propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes, such as sodium chloride and ammonium chloride.

In one embodiment, one or more of catechol, resorcinol and hydroxyquinone may be added to the conductive cathodic medium. In one
5 embodiment, the one or more of catechol, resorcinol and hydroxyquinone are present in an amount ranging from about 0.1 mg/l to about 10 g/l of the conductive cathodic medium. In another embodiment, the one or more of catechol, resorcinol and hydroxyquinone are present in an amount ranging from about 0.5 mg/l to about 1 g/l of the conductive cathodic medium.. In another
10 embodiment, the one or more of catechol, resorcinol and hydroxyquinone are present in an amount ranging from about 0.001 mg/l to about 100 mg/l of the conductive cathodic medium..

ACqua™ 220 is another lubricant additive which may be suitably included in the conductive cathodic medium 124 in the cathodic chamber. ACqua™ 220
15 is an aqueous dispersion of the zinc salt of an ethylene-acrylic copolymer, available from Michelman, Inc., Cincinnati, Ohio. In one embodiment, the ACqua™ 220 is present in an amount ranging from about 0.1 vol% to about 50 vol% of the conductive cathodic medium. In another embodiment, the ACqua™ 220 is present in an amount ranging from about 0.5 vol% to about 10 vol% of the
20 conductive cathodic medium. In another embodiment, the ACqua™ 220 is present in an amount ranging from about 1 vol% to about 5 vol% of the conductive cathodic medium. Other ACqua™ may also be useful as an additive.

In one embodiment, the conductive cathodic medium 124 in the cathodic chamber 114 contains at least one organic or inorganic compound which would
25 oxidize if in the conductive anodic medium 120. In one embodiment, the organic or inorganic compound is one of the foregoing additives in the conductive cathodic medium 124. In one embodiment, the at least one organic or inorganic compound in the conductive cathodic medium may be oxidized during the operation. This oxidation, if it occurs, is a result of the treatment process applied

ATOTP0107A

to the metal surface, and is not the direct result of oxidation by, e.g., oxygen generated by electrical current passing from the anode into the conductive anodic medium 120 in the anodic chamber 112. Thus, in one embodiment, any such oxidation is confined to the cathodic chamber 114, and in another
5 embodiment, any such oxidation is confined to a region near the metal surface to be treated, as opposed to the conductive cathodic medium 124 as a whole, or as opposed to a region near the divider, or as opposed to in the anodic chamber 112.

The conductive cathodic medium may be prepared by simply dissolving
10 the silica-containing mineral composition, together with any optionally present acid, base, buffering agents, additives, lubricants and any other ingredients in water, with appropriate temperature control as needed to facilitate dissolution.

In one embodiment, it is helpful to prepare the cathodic medium, when it will include both a LUDOX® colloidal silica and a silicate, to combine
15 substantially all of the water with the silicate, mix this thoroughly, and then add the LUDOX®. The resulting dispersion is slightly hazy. If both ingredients are combined with water at or near the same time, the resulting dispersion may be white and/or cloudy. It does not appear that any performance difference results between the media prepared by these two methods.

DIVIDER

In one embodiment, the divider comprises at least one of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode-conforming ion-selective membrane and a porous ceramic such as used in a
25 Daniel cell.

In one embodiment, membranes have been found to be useful as the divider. In various embodiments, the ion-selective membrane may be anionic, cationic, bipolar or charge-mosaic type membrane. The anionic membrane may also be referred to as an anion-exchange membrane, and the cationic

membrane may also be referred to as a cationic-exchange membrane. A bipolar membrane is an ion-exchange membrane having a structure in which a cationic membrane and an anionic membrane are attached together. A charge-mosaic membrane is composed of a two-dimensional or three-dimensional alternating cation- and anion-exchange channels throughout the membrane. In one embodiment, a combination of an anionic and a cationic membrane is used, with the anionic-selective membrane on the anode side and the cationic-selective membrane on the cathode side. In another embodiment, a combination of an anionic and a cationic membrane is used, with the cationic-selective membrane on the anode side and the anionic-selective membrane on the cathode side. In such combinations of anionic and cationic, the membranes are separated at least slightly during use, in distinction to a bipolar membrane, in which the two membranes are attached together. In one embodiment, the bipolar ion-selective membrane is disposed with its cationic side toward the cathode and its anionic side towards the anode, and in another embodiment, in the opposite configuration. Any known anionic, cationic, bipolar or charge-mosaic membrane may be used, and appropriate membranes may be selected from those known in the art.

Exemplary ion-selective membranes can be made from materials such as NAFION®, perfluorosulfonate ionomers and polyperfluorosulfonic acid; ethylene-styrene interpolymers (ESI) available from Dow Chemical; sulfonated polyarylether ketone, such as VICTREX® PEEK™, polybenzimidazole, available as PBI® from Celanese GmbH.

In one embodiment, a microporous material may also be used as the divider. For example, in one embodiment, the porous ceramics such as those used in Daniel cells may be used as the divider in the present invention.

In one embodiment, the divider may be prepared by a method such as that disclosed in U.S. Patent No. 5,590,383, or any of those disclosed in the background section of this patent. The disclosures of U.S. Patent No. 5,590,383

relating to microporous membranes is incorporated herein by reference, including in particular the book by Ramesh Bhawe, Inorganic Membranes (van Nostrand, 1991) and the article by Y.S. Lin and A.J. Burggraaf, J. Amer. Ceram. Soc., Vol. 4, 1991, p. 219.

5 In one embodiment, the divider may be a salt bridge or a sol-gel bridge. A salt bridge can provide the electric connection between the anodic chamber and the cathodic chamber while keeping the two chambers separated. The salt bridge allows electrons to transfer between the two chambers. The salt bridge may contain, for example, NaCl, KCl, KNO₃, or other salts such as alkaline, alkaline earth and transition metal salts.

10 In one embodiment, the sol-gel bridge may include, for example, a silicate sol-gel with a conductive medium attached, adhered or bonded thereto, the conductive medium including, for example, graphite or a conductive polymer as noted below, such as polyaniline or polyvinylpyridine.

15 In other embodiments, the divider may be a coating on the anode which would avoid oxidation of species in the surrounding medium. An example of such is shown in Fig. 3. The coating may be, for example, one of the polymeric materials disclosed above for use as an ion-selective membrane, or may be a porous ceramic material.

20 In one embodiment, the divider may be any of those described above configured as a container disposed relatively close to, but not in contact with, the anode. An example of such is shown in Figs. 4 and 5.

25 In one embodiment, when the electrochemical cell is operated with an uncoated steel anode with a constant potential applied across the electrochemical cell, substantially no loss of current flow is observed and substantially no anode residue is produced after 30 minutes. In one embodiment, in operation the anode remains substantially free of accumulation of foreign materials for a period of about 24 hours or more, and in another embodiment, for a period of about 48 hours or more of operation of the

ATOTP0107A

apparatus. Such foreign materials would include, for example, products of oxidation of materials in the anodic medium, which might result from oxidation by oxygen generated at the anode. As is known in the art, when a current is applied at the anode, electrons entering an aqueous solution from the anode hydrolyze water and generate oxygen gas at or near the anode. In the absence of the divider of the present invention, such oxygen causes oxidation of oxidizable organic and/or inorganic species present in the medium in which the anode is placed.

In one embodiment, the divider is other than a coating on the cathode. Since the cathode in most embodiments is the metal surface to be treated, the metal surface needs to be exposed to the silicate or other treatment materials in solution, so in such embodiment, having the membrane disposed on or very close to the cathode would not facilitate the desired reaction.

In one embodiment, the divider comprises a sol-gel, and in another embodiment a sol-gel membrane. A sol-gel is a colloidal suspension of particles of silica, alumina or a combination of silicon-based material or alumina with organic compounds, that is gelled to form a solid. The resulting porous gel can be formed as a membrane and used directly as the divider or may be first chemically modified. In one embodiment, a sol-gel membrane which is an organic-inorganic hybrid, which has been referred to as a ceramer, may be employed as the divider. For example, TEOS (tetraethylorthosilicate) may be coupled with polymers such as poly(methyl) methacrylate, poly(vinyl acetate), poly(vinyl pyrrolidone), poly(N,N-dimethylamide), polyaniline, polyvinylpyridine and graphite, and these may be made into films or membranes suitable for use as the divider. Other known sol-gel materials may be used as well. Other conductive polymers which may possibly be used with the sol-gel membranes as a divider include, for example, 3,4-polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS); polyvinylpyrrolidone (PVP), poly(vinyl pyridine-co-vinyl acetate) (PVPy-VAc), polymethacrylic acid (PMAA), poly

(hydroxyethylacrylate-co-methacrylic acid) (PHEA-MAA) and poly (2-hydroxyethyl methacrylate) (PHEMA); polyvinylbutyral (PVB). Other known conductive polymers may be used in conjunction with porous membranes as a divider in other embodiments.

5 Fig. 2 is a schematic depiction of an apparatus 200 for electrolytically treating a metal surface, in accordance with another embodiment of the present invention. The apparatus 200 includes an electrolytic cell 210, having an anodic chamber 212 and a cathodic chamber 214. The anodic chamber 212 is separated from the cathodic chamber 214 by a divider 216. The divider 216
10 allows electrical current and, in some embodiments, allows selected ions to pass through the divider 216, but prevents the passage of other ions and molecules. The divider 216 may be formed of any of the materials disclosed above with regard to the first embodiment.

 As shown in Fig. 2, in the anodic chamber 212 there is disposed an anode
15 218, which is immersed in a conductive anodic medium 220. The anode 218 in this embodiment is a conformal anode, in which the conformal anode 218 at least partially surrounds and/or conforms to the shape of the divider 216. Although shown as partially surrounding the divider 216, in one embodiment the conformal anode 218 may surround the divider 216, either as a band (i.e.,
20 covering the sides and having an open top and bottom) or as a partial enclosure (i.e., surrounding the sides and the bottom but with an open top). These alternate embodiments are not shown, but should be within the skill in the art.

 As noted with regard to the first embodiment, in accordance with one embodiment of the invention, the anode 218 may be formed of an active,
25 inexpensive metal such as iron, etc. In accordance with this embodiment of the present invention, because the anodic chamber 212 is separated from the cathodic chamber 214, it is not necessary that the anode be coated with or be formed of an inert metal, as in the prior art.

ATOTP0107A

The anodic chamber 212 contains a conductive anodic medium 220. The conductive anodic medium 220 may be acidic, neutral or basic and may have any of the pH values disclosed above with regard to the first embodiment. The conductive anodic medium 220 contains suitable acids, bases, salts and/or buffering agents to attain the selected pH. Persons of ordinary skill in the art can determine and select the appropriate combination of acids, bases, salts and/or buffering agents to attain the selected pH.

As described in above, in one embodiment, the conductive anodic medium 220 in the anodic chamber 212 is free of oxidizable organic additives.

As shown in Fig. 2, in the cathodic chamber 214 there is disposed a container 222, which is at least partially immersed in a conductive cathodic medium 224. The container 222 may be a barrel or other enclosure as is known in the electrodeposition arts for treating a plurality of relatively small parts, in which the container rotates, oscillates or otherwise moves to ensure uniform exposure of the parts to the electrolytic medium. In one embodiment, the container 222 includes a non-conductive surface, but contains inside the barrel conductive metal parts for treatment in accordance with the present invention. As noted above, the conductive metal parts in the barrel 222 act as the cathode in the apparatus shown in Fig. 2. In accordance with an embodiment of the present invention, the conductive cathodic medium 224 includes a silica compound, as described above. The container 222 is depicted in Fig. 2 in the form of an oblong or elliptical shape, but this embodiment of the invention is not limited to such a shape or any shape container in particular. As noted above, the container may be any container which is capable of exposing the parts inside the container to the conductive cathodic medium 224 in a way which results in the formation of a regular, even deposit on the surface of the parts. As in all embodiments of the present invention, the parts may comprise any kind of metal or conductive objects.

The conductive cathodic medium 224, as noted, includes a silica compound. The silica compound may be electrolytically deposited on the metal surface of the parts in the barrel 222, in order to treat the metal surface. In one embodiment, the treating is passivating the metal surface, and in another
5 embodiment, the treating is priming the metal surface. In other embodiments, other suitable treatments may be applied to the metal surface, as known in the art.

The conductive cathodic medium 224 in this embodiment may include any of the silica compounds disclosed above with regard to the first embodiment, and
10 are not repeated here for brevity.

The embodiment illustrated in Fig. 2 depicts both the conformal anode 218 and the barrel 222, used together with the divider 216 to which the conformal anode 218 conforms, but it is not so limited. In one embodiment, the barrel may be disposed in the cathodic chamber of an apparatus such as shown
15 in Fig. 1. In another embodiment, a conformal anode is used surrounding a divider similar to the divider 216, but in which one or more objects such as the object 122 are suspended as the cathode(s).

In one embodiment, the conductive cathodic medium 224 in the cathodic chamber 214 contains at least one organic or inorganic compound which would
20 oxidize if in the conductive anodic medium 220. In one embodiment, the organic or inorganic compound is one of the foregoing additives in the conductive cathodic medium 224. In one embodiment, the at least one organic or inorganic compound in the conductive cathodic medium may be oxidized during the operation. In one embodiment, such oxidation, if it occurs, is a result of the
25 treatment process applied to the metal surface, and is not the direct result of oxidation by, e.g., oxygen generated by electrical current passing from the anode into the conductive anodic medium 220 in the anodic chamber 212. Thus, in one embodiment, any such oxidation is confined to the cathodic chamber 214, and in another embodiment, any such oxidation is confined to a region near the metal

surface to be treated, as opposed to the conductive cathodic medium 224 as a whole, or as opposed to a region near the divider, or as opposed to in the anodic chamber 212.

Fig. 3 illustrates yet another embodiment of the present invention. Fig. 3 is a schematic depiction of an apparatus 300 for electrolytically treating a metal surface, in accordance with another embodiment of the present invention. The apparatus 300 includes an electrolytic cell 310, having a cathodic chamber 314, but no separate anodic chamber. The apparatus 300 includes an anode 318 and a divider 316. In this embodiment, the anode 318 is separated from the cathodic chamber 314 by the divider 316. In this embodiment, the divider surrounds, and in one embodiment, is applied to the surface of, the anode 318. The divider 316 allows electrical current and, in some embodiments, allows selected ions to pass through the divider 316, but prevents the passage of other ions and molecules. The divider 316 may be formed of any of the materials disclosed above with regard to the first embodiment.

As noted with regard to the first and second embodiments, in accordance with one embodiment of the invention, the anode 318 may be formed of an active, inexpensive metal such as iron, etc. In accordance with this embodiment of the present invention, because the anode is covered or coated with the divider 316, it is not necessary for it to be coated with or be formed of an inert metal, as in the prior art.

Other elements of the electrolytic cell 310 of this embodiment are substantially the same as described for the first and second embodiments, so the description thereof is not repeated here.

Fig. 4 illustrates yet another embodiment of the present invention. Fig. 4 is a schematic depiction of an apparatus 400 for electrolytically treating a metal surface, in accordance with another embodiment of the present invention. The apparatus 400 includes an electrolytic cell 410, having a cathodic chamber 414, and a greatly reduced anodic chamber 412, which contains an conductive anodic

medium 420. The apparatus 400 includes an anode 418 and the divider 416. As shown in Fig. 4, the anodic chamber 412 is defined by a divider 416, which forms a container in which the anode 418 is disposed. In this embodiment, the anode 418 and the anodic chamber 412 are separated from the cathodic chamber 414 by the divider 416. In this embodiment, the divider surrounds, and in one embodiment, forms a container around, the anode 418. The divider 416 allows electrical current and, in some embodiments, allows selected ions to pass through the divider 416, but prevents the passage of other ions and molecules. The divider 416 may be formed of any of the materials disclosed above with regard to the first embodiment.

As noted with regard to the first and second embodiments, in accordance with one embodiment of the invention, the anode 418 may be formed of an active, inexpensive metal such as iron, etc. In accordance with this embodiment of the present invention, because the anode is surrounded or contained by the divider 416, it is not necessary for it to be coated with or be formed of an inert metal, as in the prior art.

As noted with respect to the first and second embodiments, in this fourth embodiment, in one embodiment, the conductive cathodic medium 424 in the cathodic chamber 414 contains at least one organic or inorganic compound which would oxidize if in the conductive anodic medium 420. The same description applies to this fourth embodiment, but is not repeated here for brevity.

Other elements of the electrolytic cell 410 of this embodiment are substantially the same as described for the first, second and third embodiments, so the description thereof is not repeated here.

Fig. 5 is an enlarged view of the container formed by the divider 416, and which surrounds the anode 418. As shown in Fig. 5, the anodic chamber 412 is defined by a divider 416, which forms the container which holds the conductive anodic medium 420 and in which the anode 418 is disposed.

As shown in Fig. 4, the container formed by the divider 416, as with the divider 116, for example, separates the anode 418 and the conductive anodic medium 420 from the conductive cathodic medium 424. Thus, in one embodiment, the upper edges of the container formed by the divider 416 extend above the liquid level of the conductive cathodic medium 424. In another embodiment, not shown, the container formed by the divider 416 may completely enclose the anode 418 and the conductive anodic medium 420. In this latter embodiment, the sides of the container formed by the divider 416 would extend above the anode 418 and completely enclose it. In this embodiment, the anode 418 and the container formed by the divider 416 could be submerged in the conductive cathodic medium 424.

In one embodiment, the conductive cathodic medium 114, 214, 314 or 414 in the cathodic chamber further comprises a lubricant. In one embodiment, the lubricant comprises one or more of a polyethylene wax, PTFE, a hydrocarbon oil or a vegetable oil, a chlorinated paraffin, a phosphate ester, a sulfurized oil, a sulfurized fat, a poly- α -olefin, a polyglycol, and a carboxylic ester. In other embodiments, other known lubricants may be included in the conductive cathodic medium.

In one embodiment, a lubricant is added to assist in obtaining a consistent, uniform surface on the metal surface. In one embodiment, the lubricant is added to assist in obtaining a coefficient of friction which results in a desirable torque-tension relationship. In one embodiment, the lubricant is added to assist in obtaining an optimum lubricity so that in post-forming deformation, such as bending of the metal, damage to coatings on the metal surface is avoided or substantially reduced. For example, industry standards, such as GMW 3044 and Ford WZ100 and WZ101 relate to torque-tension requirements for metals which may include a metal surface treated in accordance with an embodiment of the present invention. In one embodiment, the lubricants contribute to torque retainment, an important safety-related feature.

ATOTP0107A

The conductive cathodic medium 114, 214, 314 or 414 in the cathodic chamber may further comprise other organic or inorganic compounds. Such organic compounds may include, for example, alkanes, haloalkanes, alcohols, ethers, thiols, alkenes, alkynes, aromatics, aldehydes, ketones, carboxylic acids, alkanoyl halides, anhydrides, esters, amides, nitriles, amines, inorganic complexes and inorganic ions. These compounds are examples of compounds which, if exposed to the anode in a conventional apparatus or in the anodic medium, would be subject to oxidation or other decomposition, resulting in the negative effects sought to be avoided by the present invention.

In the prior art, in which a similar process was carried out in a single, undivided electrolytic chamber, the presence of organic or inorganic compounds and lubricants, such as those listed above, in the electrolytic chamber, could result in one or more of several problems. The organic or inorganic compounds were likely to be oxidized by oxygen generated at the anode and/or were likely to accumulate in decomposed form on the anode. The presence of the oxidized materials in the electrolytic medium could result in additional problems such as unwanted chemical reactions with other ingredients, unwanted chemical reactions with and/or deposition upon the cathode material, and reduction in efficiency of the process due to interference with electrolytic current flow. Accumulation of decomposition products on the anode could result in reduction in efficiency of the process due to interference with electrolytic current flow, chemical reaction with the anode material, and need to clean frequently the anode to remove such decomposition products, which would result in downtime and in additional exposure of personnel to the chemicals in the electrolytic medium.

The oxidizable organic or inorganic compounds, e.g., materials and additives which may be present in the conductive cathodic medium and which would be subject to oxidation in a single container electrolytic cell include, for example, organic and inorganic chelating and complexing agents, organic and

ATOTP0107A

inorganic brighteners, cross-linking additives, silanes, siloxanes and partially oxidized silicon compounds, detergents, surfactants and wetting agents, foam suppressants and similar materials known in the art for use in electrolytic treatments. In one embodiment, the oxidizable organic or inorganic compounds include any of the additives disclosed above for possible addition to the conductive cathodic medium.

In one embodiment of the present invention, one or more of these problems are substantially avoided, and in one embodiment, all of these problems are substantially avoided, as a result of the divider 116, 216, 316 and 416 in the electrochemical cell 100, 200, 300 or 400, respectively. By use of the divider, it is possible to employ a conductive anodic medium 120 or 220 or 420 which is significantly different from the conductive cathodic medium 124 or 224 in the cathodic chamber 114 or 214. For example, the conductive anodic medium may comprise a simple aqueous solution of, for example, sodium hydroxide substantially free of any organic additives, while the conductive cathodic medium may comprise, for example, a complex mixture of organic and inorganic compounds as needed for the specific treatment of the metal surface. The use of the divider allows avoidance or significant reduction of the prior art problems noted above, which result from exposure of the anode to various additives which would be present in the undivided electrolytic medium.

PROCESS

The metal surface to be treated in accordance with the present invention may be pre-treated or cleaned in accordance with conventional methods. Such methods are employed for removing oils and debris that could interfere with the treatment process. An example of a pre-treatment including, for example, hydrogen peroxide wash, and rinse with water and/or a solvent, or a hot alkali cleaning followed by a water rinse. The metal surface can also be pre-treated in accordance with other conventional methods such as phosphating, chromating,

ATOTP0107A

molybdating, vanadating, zirconating, and titanating, among other metal treatment processes.

The following is a list of parameters which may be varied for tailoring the inventive process to obtain a desirable treatment of the metal surface:

- 5 1. Voltage applied
2. Current density applied
3. Time of current flow
4. Concentration and type(s) of silica-containing mineral composition in cathodic medium
- 10 5. Concentration and type(s) of other anions in either anodic or cathodic medium
6. Concentration and type(s) of other cations in either anodic or cathodic medium
7. Apparatus or cell design or configuration, including divider configuration
- 15 8. Composition of the anode
9. Composition of the cathode
10. Temperature
11. Pressure (usually atmospheric)
12. Concentration and type(s) of additives in the cathodic medium

20

The specific ranges of the above and any other parameters depend on the substrate to be deposited on and the intended composition to be deposited.

Items 4-6 and 12 can be especially effective in tailoring the chemical characteristics of the coating. Items 1-3, 10 and 11 can affect the deposition time and physical characteristics such as the coating thickness. Items 7 and 8 can be appropriately and more easily modified as a result of the invention. The differing types of additional anions and cations have been disclosed above, and can further comprise Group I metals, Group II metals, transition and rare earth metal oxides, oxyanions such as molybdate, phosphate, titanate, others such as

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ATOTP0107A

boron nitride, silicon carbide, aluminum nitride, silicon nitride, and mixtures of any of the foregoing, among others. Item 9 can affect choices made for all the other variables.

5 In one embodiment, the present invention relates to a process of treating a metal surface, including steps of providing a metal surface; providing an electrochemical cell, in which the electrochemical cell includes an anodic chamber having an anode disposed therein, and containing a conductive anodic medium; a cathodic chamber in which the metal surface may be disposed as a cathode, and containing a conductive cathodic medium comprising a silica
10 compound; and a divider disposed to separate the anodic chamber from the cathodic chamber; applying an electric current to the electrochemical cell at a rate and period of time sufficient to treat the metal surface. In one embodiment, the treating includes depositing a coating or film of a silicon-containing mineral. In one embodiment, the treating is passivating or priming the metal surface.

15 In one embodiment, the electrical current is applied to the electrochemical cell as a continuous DC current. In another embodiment, the electrical current is applied to the electrochemical cell as a pulsed DC current. In another embodiment, the electrical current is applied to the electrochemical cell as a pulsed DC current with periodic reversal. In one embodiment, the pulsed DC
20 current is applied to the electrochemical cell as a square wave, as a sawtooth wave, or in other waveforms known in the art. In another embodiment, the electrical current is applied to the electrochemical cell as pulse rectification with periodic reversal.

25 In one embodiment, the conductive anodic medium has a basic pH. In one embodiment, the conductive anodic medium is substantially free of oxidizable organic additives. Due to the divider, which in one embodiment is at least one of a salt bridge, an ion-selective membrane, a sol-gel, an ion-selective anode coating, an anode conforming ion-selective membrane or a porous ceramic, the oxidizable organic or inorganic materials which may be present in

the conductive cathodic medium are not oxidized by the anode in the process. Thus, for example, in one embodiment the conductive cathodic medium further comprises a lubricant. In one embodiment, the lubricant includes one or more of a polyethylene wax, PTFE and a hydrocarbon or vegetable oil.

5 As a further result of using the divider, the anode may be made of or include an active metal, and may be free of protection by a noble metal. Thus, in one embodiment, the anode includes an uncoated active metal.

10 As a result of using the divider, the electrochemical cell may be operated with an uncoated steel anode applying a current across the electrochemical cell without loss of current flow for periods of time which were not previously attainable. In one embodiment, substantially no loss of current flow is observed and substantially no anode residue is produced after 30 minutes of operation with an uncoated steel anode with a constant potential applied. In another
15 embodiment, during the time the current is applied, the anode remains substantially free of accumulation of foreign materials. In another embodiment, during the time the current is applied, organic or inorganic chemical species in the conductive cathodic medium remain substantially free of oxidation by oxygen generated at the anode.

20 **EXAMPLES**

The following examples are provided to further illustrate embodiments of the present invention and are not intended to limit the invention in any way.

25 Except as otherwise stated, all examples are carried out in an electrochemical cell similar to that shown in Fig. 1. "Standard IEP" is a proprietary Inorganic Electrophoretic Passivation material commercially available from Elisha Technologies Co., Moberly, Missouri, under the trade name Elisha CM Treatment Solution. This solution is believed to contain from about 5 to about 50 wt% of a silica-containing mineral composition, such as PQN-grade silica and LUDOX® AM-30 colloidal silica, as disclosed in U.S. Patent No.

ATOTP0107A

6,455,100, which is incorporated herein by reference for its teachings relating to silica-containing mineral compositions and deposition thereof.

Example 1

5 Divider: cationic selective membrane
 Anode: iron
 Anodic medium: 6.25 wt% NaOH in water
 Cathode: zinc
10 Cathodic medium: Std. IEP + 0.001 g/l catechol
 Temp.: RT
 Time: 10 min.
 Begin voltage: 12 v. End voltage: 12 v.
 Begin current: 0.5 amp End current: 0.5 amp

15 Example 2

 Divider: anionic selective membrane
 Anode: iron
 Anodic medium: 6.25 wt% NaOH in water
20 Cathode: zinc
 Cathodic medium: Std. IEP + 0.001 g/l catechol
 Temp.: RT
 Time: 10 min.
 Begin voltage: 12 v. End voltage: 12 v.
25 Begin current: 0.5 amp End current: 0.5 amp

Example 3

 Divider: anionic selective membrane
 Anode: iron
 Anodic medium: 6.25 wt% NaOH in water
30 Cathode: zinc
 Cathodic medium: Std. IEP + 0.001 g/l catechol + 1%v. ACqua 220
 Temp.: RT
 Time: 10 min.
 Begin voltage: 12 v. End voltage: 12 v.
35 Begin current: 0.5 amp End current: 0.5 amp

Some foaming is observed at the cathode.

ATOTP0107A

Example 4

	Divider:	anionic selective membrane		
	Anode:	nickel		
5	Anodic medium:	6.25 wt% NaOH in water		
	Cathode:	zinc		
	Cathodic medium:	Std. IEP + 0.001 g/l catechol + 1%v. ACQUA 220		
	Temp.:	RT		
	Time:	30 min.		
10	Begin voltage:	13 v.	End voltage:	13 v.
	Begin current:	1.1 amp	End current:	1.1 amp

Example 5

	Divider:	anionic selective membrane		
	Anode:	iron		
15	Anodic medium:	6.25 wt% NaOH in water		
	Cathode:	iron		
	Cathodic medium:	Std. IEP + 0.001 g/l catechol + 1%v. ACqua 220		
	Temp.:	RT		
	Time:	30 min.		
20	Begin voltage:	13 v.	End voltage:	13 v.
	Begin current:	1 amp	End current:	1 amp

Example 6

	Divider:	anionic selective membrane		
25	Anode:	iron Hull cell plate		
	Anodic medium:	6.25 wt% NaOH in water		
	Cathode:	Zn plated Hull cell plate		
	Cathodic medium:	Std. IEP		
	Temp.:	115°F (~46°C)		
30	Time:	10 min.		
	Begin voltage:	12 v.	End voltage:	12 v.
	Begin current:	1.25 amp	End current:	1.25 amp

35 In each of the foregoing Examples 1-6, the treatment process proceeds without decrease in the applied current, without buildup of deposits on the anode, and without detectable oxidation of any species in the conductive cathodic medium. In each of the foregoing Examples 1-6, the treatment process results in the formation of a silica-containing mineral deposit on the surface of the cathode.

ATOTP0107A

The silica-containing mineral deposit formed in each of the foregoing Examples 1-6 is similar to that obtained by the process disclosed in U.S. Patent No. 6,455,100.

5 Comparative Example 1

	Divider:	none		
	Anode:	nickel		
	Anodic medium:	none - carry out in single chamber		
	Cathode:	Zn		
10	Cathodic medium:	Std. IEP + 0.001 g/l catechol + 1%v. ACqua 220		
	Temp.:	RT		
	Time:	30 min.		
	Begin voltage:	13 v.	End voltage:	13 v.
	Begin current:	1.1 amp	End current:	<0.5 amp

15 A white residue accumulates on the anode.

As shown by Comparative Example 1, when the treatment is carried out in a single chamber, a reduction in current is observed, which indicates oxidation of organic species by oxygen at the anode and accumulation of decomposition products on the anode, either or both of which contribute to the loss of current flow.

20

Comparative Example 2

	Divider:	none		
25	Anode:	iron		
	Anodic medium:	none - carry out in single chamber		
	Cathode:	Zn		
	Cathodic medium:	Std. IEP + 0.001 g/l catechol + 1%v. ACqua 220		
	Temp.:	RT		
30	Time:	30 min.		
	Begin voltage:	13 v.	End voltage:	13 v.
	Begin current:	1.5 amp	End current:	0.9 amp

Black residue accumulates on the anode.

ATOTP0107

As shown by Comparative Example 2, when the treatment is carried out in a single chamber, a reduction in current is observed, which indicates oxidation of organic species by oxygen at the anode and accumulation of decomposition products on the anode, either or both of which contribute to the loss of current flow. In this example, accumulation of black residue on the anode indicates that oxidation is occurring at or near the anode.

While the invention has been explained in relation to various of its embodiments, it is to be understood that other modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.